

## IMPACT-MODIFIED COMPOSITIONS AND METHOD

## BACKGROUND OF THE INVENTION

[0001] The present invention relates to compositions comprising a polycarbonate and a rubber modified thermoplastic resin. Compositions comprising a polycarbonate and a rubber modified thermoplastic resin are known in the art. These compositions often have a problem with color formation during processing or during use in applications at high temperature. A problem to be solved is to devise compositions comprising a polycarbonate and a rubber modified thermoplastic resin which exhibit color stability under conditions of high temperature.

## BRIEF DESCRIPTION OF THE INVENTION

[0002] The present inventors have discovered compositions comprising a polycarbonate and a rubber modified thermoplastic resin which show a surprising decrease in color formation under high temperature conditions, such as during molding or other thermal processing. The compositions also possess an attractive balance of other physical properties.

[0003] In a particular embodiment the present invention relates to a composition comprising (i) at least one polycarbonate; (ii) optionally, at least one additional thermoplastic resin different from polycarbonate; and (iii) at least one rubber modified thermoplastic resin comprising a discontinuous elastomeric phase dispersed in a rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is grafted to the elastomeric phase, and wherein the rigid thermoplastic phase comprises structural units derived from at least one vinyl aromatic monomer, at least one monoethylenically unsaturated nitrile monomer, and at least one monomer selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers.

[0004] In other embodiments the present invention relates to articles made from the composition and a method to prepare the composition. Various other features, aspects, and advantages of the present invention will become more apparent with reference to the following description and appended claims.

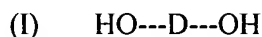
## DETAILED DESCRIPTION OF THE INVENTION

[0005] In the following specification and the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings.

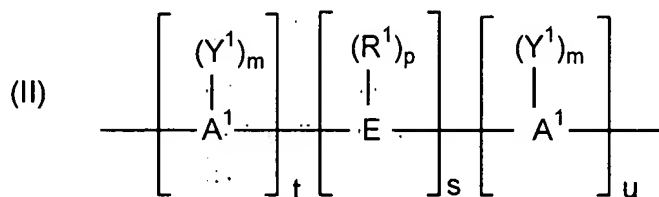
The singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not. As used herein the term "polycarbonate" refers to polycarbonates comprising structural units derived from a carbonate precursor and at least one dihydroxy-substituted aromatic hydrocarbon, and includes copolycarbonates.

[0006] Polycarbonates useful in compositions of the present invention comprise structural units derived from at least one dihydroxy aromatic hydrocarbon. In various embodiments structural units derived from at least one dihydroxy aromatic hydrocarbon comprise at least about 60 percent of the total number of structural units derived from any dihydroxy-substituted hydrocarbon in the polycarbonates, and the balance of structural units derived from any dihydroxy-substituted hydrocarbon are aliphatic, alicyclic, or aromatic radicals.

[0007] In embodiments of the invention dihydroxy-substituted aromatic hydrocarbons from which structural units of polycarbonates may be derived comprise those represented by the formula (I):



wherein D is a divalent aromatic radical. In some embodiments, D has the structure of formula (II):



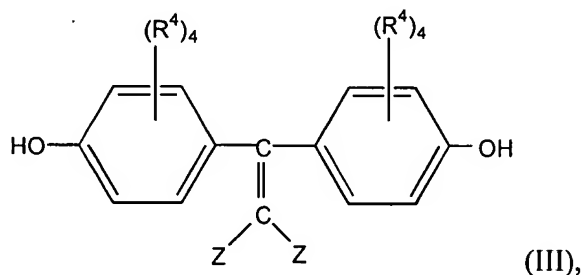
wherein  $A^1$  represents an aromatic group including, but not limited to, phenylene, biphenylene, naphthylene and the like. In some embodiments E may be an alkylene or alkylidene group including, but not limited to, methylene, ethylene, ethylidene, propylene, propylidene, isopropylidene, butylene, butylidene, isobutylidene, amylene, amylidene, isoamylidene and the like. In other embodiments when E is an alkylene or alkylidene group, it may also consist of two or more alkylene or alkylidene groups connected by a moiety different from alkylene or alkylidene, including, but not limited to, an aromatic linkage; a tertiary nitrogen linkage; an ether

linkage; a carbonyl linkage; a silicon-containing linkage, silane, siloxy; or a sulfur-containing linkage including, but not limited to, sulfide, sulfoxide, sulfone, and the like; or a phosphorus-containing linkage including, but not limited to, phosphinyl, phosphonyl, and the like. In other embodiments E may be a cycloaliphatic group including, but not limited to, cyclopentylidene, cyclohexylidene, 3,3,5-trimethylcyclohexylidene, methylcyclohexylidene, 2-[2.2.1]-bicycloheptylidene, neopentylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene, and the like; a sulfur-containing linkage, including, but not limited to, sulfide, sulfoxide or sulfone; a phosphorus-containing linkage, including, but not limited to, phosphinyl or phosphonyl; an ether linkage; a carbonyl group; a tertiary nitrogen group; or a silicon-containing linkage including, but not limited to, silane or siloxy.  $R^1$  independently at each occurrence comprises a monovalent hydrocarbon group including, but not limited to, alkenyl, allyl, alkyl, aryl, aralkyl, alkaryl, or cycloalkyl. In various embodiments a monovalent hydrocarbon group of  $R^1$  may be halogen-substituted, particularly fluoro- or chloro-substituted, for example as in dichloroalkylidene, particularly gem-dichloroalkylidene.  $Y^1$  independently at each occurrence may be an inorganic atom including, but not limited to, halogen (fluorine, bromine, chlorine, iodine); an inorganic group containing more than one inorganic atom including, but not limited to, nitro; an organic group including, but not limited to, a monovalent hydrocarbon group including, but not limited to, alkenyl, allyl, alkyl, aryl, aralkyl, alkaryl, or cycloalkyl, or an oxy group including, but not limited to,  $OR^2$  wherein  $R^2$  is a monovalent hydrocarbon group including, but not limited to, alkyl, aryl, aralkyl, alkaryl, or cycloalkyl; it being only necessary that  $Y^1$  be inert to and unaffected by the reactants and reaction conditions used to prepare the polymer. In some particular embodiments  $Y^1$  comprises a halo group or  $C_1$ - $C_6$  alkyl group. The letter "m" represents any integer from and including zero through the number of replaceable hydrogens on  $A^1$  available for substitution; "p" represents an integer from and including zero through the number of replaceable hydrogens on E available for substitution; "t" represents an integer equal to at least one; "s" represents an integer equal to either zero or one; and "u" represents any integer including zero.

[0008] In dihydroxy-substituted aromatic hydrocarbons in which D is represented by formula (II) above, when more than one  $Y^1$  substituent is present, they may be the same or different. The same holds true for the  $R^1$  substituent. Where "s" is zero in formula (II) and "u" is not zero, the aromatic rings are directly joined by a covalent bond with no intervening alkylidene or other bridge. The positions of the hydroxyl groups and  $Y^1$  on the aromatic nuclear residues  $A^1$  can be varied in the ortho, meta, or

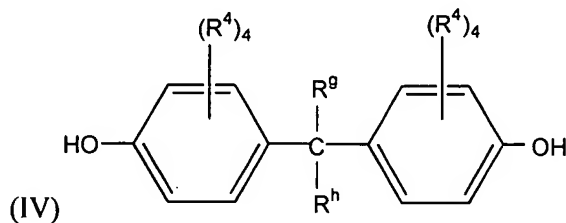
para positions and the groupings can be in vicinal, asymmetrical or symmetrical relationship, where two or more ring carbon atoms of the hydrocarbon residue are substituted with  $Y^1$  and hydroxyl groups. In some particular embodiments the parameters "t", "s", and "u" each have the value of one; both  $A^1$  radicals are unsubstituted phenylene radicals; and E is an alkylidene group such as isopropylidene. In some particular embodiments both  $A^1$  radicals are p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

[0009] In some embodiments of dihydroxy-substituted aromatic hydrocarbons E may be an unsaturated alkylidene group. Suitable dihydroxy-substituted aromatic hydrocarbons of this type include those of the formula (III):



where independently each  $R^4$  is hydrogen, chlorine, bromine or a  $C_{1-30}$  monovalent hydrocarbon or hydrocarbonoxy group, each Z is hydrogen, chlorine or bromine, subject to the provision that at least one Z is chlorine or bromine.

[0010] Suitable dihydroxy-substituted aromatic hydrocarbons also include those of the formula (IV):



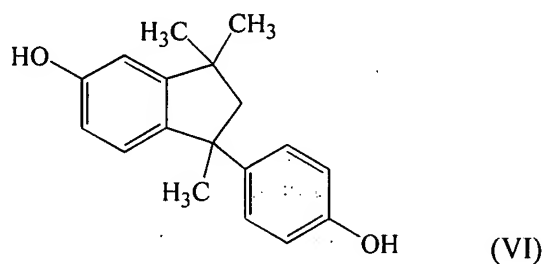
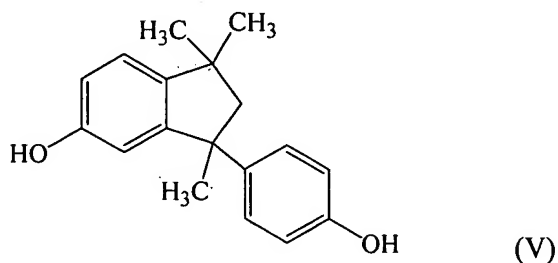
5 where independently each  $R^4$  is as defined hereinbefore, and independently  $R^g$  and  $R^h$  are hydrogen or a  $C_{1-30}$  hydrocarbon group.

[0011] In some embodiments of the present invention, dihydroxy-substituted aromatic hydrocarbons that may be used comprise those disclosed by name or formula (generic or specific) in U.S. Patent Nos. 2,991,273, 2,999,835, 3,028,365, 3,148,172,

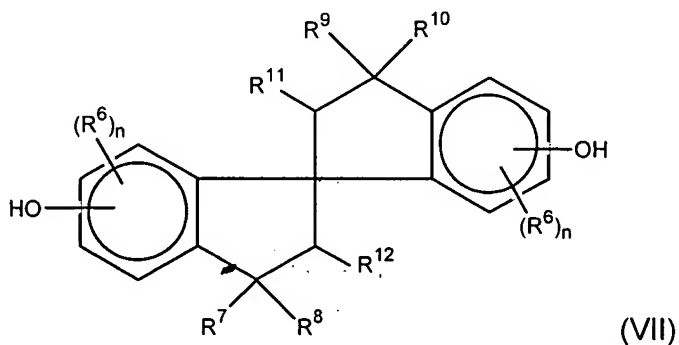
3,153,008, 3,271,367, 3,271,368, and 4,217,438. In other embodiments of the invention, dihydroxy-substituted aromatic hydrocarbons comprise bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl) ether, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, 1,4-dihydroxybenzene, 4,4'-oxydiphenol, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol; 4,4'-bis(3,5-dimethyl)diphenol, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane; 4,4-bis(4-hydroxyphenyl)heptane; 2,4'-dihydroxydiphenylmethane; bis(2-hydroxyphenyl)methane; bis(4-hydroxyphenyl)methane; bis(4-hydroxy-5-nitrophenyl)methane; bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane; 1,1-bis(4-hydroxyphenyl)ethane; 1,2-bis(4-hydroxyphenyl)ethane; 1,1-bis(4-hydroxy-2-chlorophenyl)ethane; 2,2-bis(3-phenyl-4-hydroxyphenyl)propane; 2,2-bis(4-hydroxy-3-methylphenyl)propane; 2,2-bis(4-hydroxy-3-ethylphenyl)propane; 2,2-bis(4-hydroxy-3-isopropylphenyl)propane; 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane; 3,5,3',5'-tetrachloro-4,4'-dihydroxyphenyl)propane; bis(4-hydroxyphenyl)cyclohexylmethane; 2,2-bis(4-hydroxyphenyl)-1-phenylpropane; 2,4'-dihydroxyphenyl sulfone; dihydroxy naphthalene; 2,6-dihydroxy naphthalene; hydroquinone; resorcinol; C<sub>1-3</sub> alkyl-substituted resorcinols; methyl resorcinol, catechol, 1,4-dihydroxy-3-methylbenzene; 2,2-bis(4-hydroxyphenyl)butane; 2,2-bis(4-hydroxyphenyl)-2-methylbutane; 1,1-bis(4-hydroxyphenyl)cyclohexane; 4,4'-dihydroxydiphenyl; 2-(3-methyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane; 2-(3,5-dimethyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane; 2-(3-methyl-4-hydroxyphenyl)-2-(3,5-dimethyl-4-hydroxyphenyl)propane; bis(3,5-dimethylphenyl-4-hydroxyphenyl)methane; 1,1-bis(3,5-dimethylphenyl-4-hydroxyphenyl)ethane; 2,2-bis(3,5-dimethylphenyl-4-hydroxyphenyl)propane; 2,4-bis(3,5-dimethylphenyl-4-hydroxyphenyl)-2-methylbutane; 3,3-bis(3,5-dimethylphenyl-4-hydroxyphenyl)pentane; 1,1-bis(3,5-dimethylphenyl-4-hydroxyphenyl)cyclopentane; 1,1-bis(3,5-dimethylphenyl-4-hydroxyphenyl)cyclohexane; bis(3,5-dimethyl-4-hydroxyphenyl) sulfoxide, bis(3,5-dimethyl-4-hydroxyphenyl) sulfone and bis(3,5-dimethylphenyl-4-hydroxyphenyl)sulfide; and the like. In a particular embodiment the dihydroxy-substituted aromatic hydrocarbon comprises bisphenol A.

[0012] In some embodiments of dihydroxy-substituted aromatic hydrocarbons when E is an alkylene or alkylidene group, said group may be part of one or more fused rings attached to one or more aromatic groups bearing one hydroxy substituent. Suitable dihydroxy-substituted aromatic hydrocarbons of this type include those containing indane structural units such as represented by the formula (V), which

compound is 3-(4-hydroxyphenyl)-1,1,3-trimethylindan-5-ol, and by the formula (VI), which compound is 1-(4-hydroxyphenyl)-1,3,3-trimethylindan-5-ol:



[0013] Also included among suitable dihydroxy-substituted aromatic hydrocarbons of the type comprising one or more alkylene or alkylidene groups as part of fused rings are the 2,2,2',2'-tetrahydro-1,1'-spirobi[1H-indene]diols having formula (VII) :



wherein each  $R^6$  is independently selected from monovalent hydrocarbon radicals and halogen radicals; each  $R^7$ ,  $R^8$ ,  $R^9$ , and  $R^{10}$  is independently  $C_{1-6}$  alkyl; each  $R^{11}$  and  $R^{12}$  is independently H or  $C_{1-6}$  alkyl; and each  $n$  is independently selected from positive integers having a value of from 0 to 3 inclusive. In a particular embodiment the 2,2,2',2'-tetrahydro-1,1'-spirobi[1H-indene]diol is 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indene]-6,6'-diol (sometimes known as "SBI"). Mixtures

comprising at least one of any of the foregoing dihydroxy-substituted aromatic hydrocarbons may also be employed.

[0014] Polycarbonates of the invention further comprise structural units derived from at least one carbonate precursor. There is no particular limitation on the carbonate precursor. Phosgene or diphenyl carbonate are frequently used. There is no particular limitation on the method for making suitable polycarbonates. Any known process may be used. In some embodiments an interfacial process or a melt transesterification process may be used.

[0015] In one embodiment of the invention the polycarbonate comprises at least one homopolycarbonate, wherein the term "homopolycarbonate" refers to a polycarbonate synthesized using only one type of dihydroxy-substituted aromatic hydrocarbon. In particular embodiments the polycarbonate comprises a bisphenol A homo- or copolycarbonate, wherein the term "copolycarbonate" refers to a polycarbonate synthesized using more than one type of dihydroxy-substituted hydrocarbon, and in particular more than one type of dihydroxy-substituted aromatic hydrocarbon. In another particular embodiment the polycarbonate comprises a linear homopolycarbonate resin derived from bisphenol A. In other embodiments the polycarbonate comprises a blend of at least one first polycarbonate with at least one other polymeric resin, examples of which include, but are not limited to, a second polycarbonate differing from said first polycarbonate either in structural units or in molecular weight or in both these parameters, or a polyester, or an addition polymer such as acrylonitrile-styrene-acrylate copolymer.

[0016] In various embodiments the weight average molecular weight of the polycarbonate ranges from about 5,000 to about 200,000. In other particular embodiments the weight average molecular weight of the polycarbonate resin is in one embodiment from about 10,000 to about 200,000 grams per mole ("g/mol"), in another embodiment from about 17,000 to about 100,000 g/mol, in another embodiment from about 18,000 to about 80,000 g/mol, in another embodiment from about 18,000 to about 40,000 g/mol, in still another embodiment from about 18,000 to about 36,000 g/mol, in still another embodiment from about 18,000 to about 30,000 g/mol, and in still another embodiment from about 18,000 to about 23,000 g/mol, all as determined by gel permeation chromatography relative to polystyrene standards. In other embodiments the weight average molecular weight of the polycarbonate ranges from about 28,000 to about 36,000 g/mol. Suitable polycarbonate resins exhibit an intrinsic viscosity in one embodiment of about 0.1 to about 1.5 deciliters per gram, in

another embodiment of about 0.35 to about 0.9 deciliters per gram, in another embodiment of about 0.4 to about 0.6 deciliters per gram, and in still another embodiment of about 0.48 to about 0.54 deciliters per gram, all measured in methylene chloride at 25°C.

[0017] In a polycarbonate-containing blend there may be an improvement in melt flow and/or other physical properties when one molecular weight grade of a polycarbonate is combined with a proportion of a relatively lower molecular weight grade of similar polycarbonate. Therefore, the present invention encompasses compositions comprising only one molecular weight grade of a polycarbonate and also compositions comprising two or more molecular weight grades of polycarbonate. When two or more molecular weight grades of polycarbonate are present, then the weight average molecular weight of the lowest molecular weight polycarbonate is in one embodiment about 10% to about 95%, in another embodiment about 40% to about 85%, and in still another embodiment about 60% to about 80% of the weight average molecular weight of the highest molecular weight polycarbonate. In one representative, non-limiting embodiment polycarbonate-containing blends include those comprising a polycarbonate with weight average molecular weight between about 18,000 and about 23,000 combined with a polycarbonate with weight average molecular weight between about 28,000 and about 36,000 (in all cases relative to polystyrene standards). When two or more molecular weight grades of polycarbonate are present, the weight ratios of the various molecular weight grades may range from about 1 to about 99 parts of one molecular weight grade and from about 99 to about 1 parts of any other molecular weight grades. In some embodiments a mixture of two molecular weight grades polycarbonate is employed, in which case the weight ratios of the two grades may range in one embodiment from about 99:1 to about 1:99, in another embodiment from about 80:20 to about 20:80, and in still another embodiment from about 70:30 to about 50:50. Since not all manufacturing processes for making a polycarbonate are capable of making all molecular weight grades of that constituent, the present invention encompasses compositions comprising two or more molecular weight grades of polycarbonate in which each polycarbonate is made by a different manufacturing process. In one particular embodiment the instant invention encompasses compositions comprising a polycarbonate made by an interfacial process in combination with a polycarbonate of different weight average molecular weight made by a melt process.



[0018] The amount of polycarbonate present in the compositions of the present invention is in one embodiment in a range of between about 5 wt.% and about 95 wt.%, in another embodiment in a range of between about 20 wt.% and about 85 wt.%, and in still another embodiment in a range of between about 25 wt.% and about 80 wt.%, based on the weight of the entire composition.

[0019] In various embodiments the compositions of the present invention comprise a rubber modified thermoplastic resin comprising a discontinuous elastomeric phase and a rigid thermoplastic phase wherein at least a portion of the rigid thermoplastic phase is grafted to the elastomeric phase. The compositions are derived from grafting at least one rubber substrate. The rubber substrate comprises the discontinuous elastomeric phase of the composition. There is no particular limitation on the rubber substrate provided it is susceptible to grafting by at least a portion of a graftable monomer. The rubber substrate typically has a glass transition temperature,  $T_g$ , in one embodiment below about 0°C, in another embodiment below about minus 20°C, and in still another embodiment below about minus 30°C.

[0020] In various embodiments the rubber substrate is derived from polymerization by known methods of at least one monoethylenically unsaturated alkyl (meth)acrylate monomer selected from  $(C_1-C_{12})$ alkyl(meth)acrylate monomers and mixtures comprising at least one of said monomers. As used herein, the terminology "monoethylenically unsaturated" means having a single site of ethylenic unsaturation per molecule, and the terminology "(meth)acrylate monomers" refers collectively to acrylate monomers and methacrylate monomers. As used herein, the terminology " $(C_x-C_y)$ ", as applied to a particular unit, such as, for example, a chemical compound or a chemical substituent group, means having a carbon atom content of from "x" carbon atoms to "y" carbon atoms per such unit. For example, " $(C_1-C_{12})$ alkyl" means a straight chain, branched or cyclic alkyl substituent group having from 1 to 12 carbon atoms per group and includes, but is not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. Suitable  $(C_1-C_{12})$ alkyl(meth)acrylate monomers include, but are not limited to,  $(C_1-C_{12})$ alkyl acrylate monomers, illustrative examples of which include ethyl acrylate, butyl acrylate, iso-pentyl acrylate, n-hexyl acrylate, and 2-ethyl hexyl acrylate; and their  $(C_1-C_{12})$ alkyl methacrylate analogs illustrative examples of which include methyl methacrylate, ethyl methacrylate, propyl methacrylate, iso-propyl methacrylate, butyl methacrylate, hexyl methacrylate, and decyl methacrylate. In a

particular embodiment of the present invention the rubber substrate comprises structural units derived from n-butyl acrylate.

[0021] In various embodiments the rubber substrate may also comprise structural units derived from at least one polyethylenically unsaturated monomer. As used herein, the terminology "polyethylenically unsaturated" means having two or more sites of ethylenic unsaturation per molecule. A polyethylenically unsaturated monomer is often employed to provide cross-linking of the rubber particles and to provide "graftlinking" sites in the rubber substrate for subsequent reaction with grafting monomers. Suitable polyethylenic unsaturated monomers include, but are not limited to, butylene diacrylate, divinyl benzene, butene diol dimethacrylate, trimethylolpropane tri(meth)acrylate, allyl methacrylate, diallyl methacrylate, diallyl maleate, diallyl fumarate, diallyl phthalate, triallyl methacrylate, triallylcyanurate, triallylisocyanurate, the acrylate of tricyclodecenylalcohol and mixtures comprising at least one of such monomers. In a particular embodiment the rubber substrate comprises structural units derived from triallylcyanurate.

[0022] In some embodiments the rubber substrate may optionally comprise structural units derived from minor amounts of other unsaturated monomers, for example those which are copolymerizable with an alkyl (meth)acrylate monomer used to prepare the rubber substrate. Suitable copolymerizable monomers include, but are not limited to,  $C_1$ - $C_{12}$  aryl or haloaryl substituted acrylate,  $C_1$ - $C_{12}$  aryl or haloaryl substituted methacrylate, or mixtures thereof; monoethylenically unsaturated carboxylic acids, such as, for example, acrylic acid, methacrylic acid and itaconic acid; glycidyl (meth)acrylate, hydroxy alkyl (meth)acrylate, hydroxy( $C_1$ - $C_{12}$ )alkyl (meth)acrylate, such as, for example, hydroxyethyl methacrylate; ( $C_4$ - $C_{12}$ )cycloalkyl (meth)acrylate monomers, such as, for example, cyclohexyl methacrylate; (meth)acrylamide monomers, such as, for example, acrylamide, methacrylamide and N-substituted-acrylamide or -methacrylamides; maleimide monomers, such as, for example, maleimide, N-alkyl maleimides, N-aryl maleimides and haloaryl substituted maleimides; maleic anhydride; vinyl methyl ether, vinyl esters, such as, for example, vinyl acetate and vinyl propionate. As used herein, the term "(meth)acrylamide" refers collectively to acrylamides and methacrylamides. Suitable copolymerizable monomers also include, but are not limited to, vinyl aromatic monomers, such as, for example, styrene and substituted styrenes having one or more alkyl, alkoxy, hydroxy or halo substituent groups attached to the aromatic ring, including, but not limited to, alpha-methyl styrene, p-methyl styrene, 3,5-diethylstyrene, 4-n-propylstyrene, vinyl

toluene, alpha-methyl vinyltoluene, vinyl xylene, trimethyl styrene, butyl styrene, t-butyl styrene, chlorostyrene, alpha-chlorostyrene, dichlorostyrene, tetrachlorostyrene, bromostyrene, alpha-bromostyrene, dibromostyrene, p-hydroxystyrene, p-acetoxystyrene, methoxystyrene and vinyl-substituted condensed aromatic ring structures, such as, for example, vinyl naphthalene, vinyl anthracene, as well as mixtures of vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers such as, for example, acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha-bromoacrylonitrile and alpha-chloro acrylonitrile. Substituted styrenes with mixtures of substituents on the aromatic ring are also suitable

[0023] The rubber substrate may be present in the rubber modified thermoplastic resin portion of the compositions of the invention in one embodiment at a level of from about 10 to about 94 percent by weight; in another embodiment at a level of from about 10 to about 80 percent by weight; in another embodiment at a level of from about 15 to about 80 percent by weight; in another embodiment at a level of from about 35 to about 80 percent by weight; in another embodiment at a level of from about 40 to about 80 percent by weight; in another embodiment at a level of from about 25 to about 60 percent by weight, and in still another embodiment at a level of from about 40 to about 50 percent by weight based on the weight of the rubber modified thermoplastic resin. In other embodiments the rubber substrate may be present in the rubber modified thermoplastic resin portion of the compositions of the invention at a level of from about 5 to about 50 percent by weight; at a level of from about 8 to about 40 percent by weight; or at a level of from about 10 to about 30 percent by weight based on the weight of the rubber modified thermoplastic resin.

[0024] There is no particular limitation on the particle size distribution of the rubber substrate (sometimes referred to hereinafter as initial rubber substrate to distinguish it from the rubber substrate following grafting). In some embodiments the rubber substrate may possess a broad particle size distribution with particles ranging in size from about 50 nanometers (nm) to about 1000nm. In other embodiments the number average particle size of the rubber substrate may be less than about 100nm. In still other embodiments the number average particle size of the rubber substrate may be in a range of between about 80nm and about 500nm. In still other embodiments the number average particle size of the rubber substrate may be in a range of between about 200nm and about 750nm. In other embodiments the number average particle size of the rubber substrate may be greater than about 400nm.

[0025] To prepare the rubber modified thermoplastic resin used in the invention, monomers are polymerized in the presence of the rubber substrate to thereby form a graft copolymer, at least a portion of which is chemically grafted to the rubber phase. Any portion of graft copolymer not chemically grafted to rubber substrate comprises the rigid thermoplastic phase. The rigid thermoplastic phase comprises a thermoplastic polymer or copolymer that exhibits a glass transition temperature ( $T_g$ ) in one embodiment of greater than about 25°C, in another embodiment of greater than or equal to 90°C, and in still another embodiment of greater than or equal to 100°C.

[0026] In a particular embodiment the rigid thermoplastic phase of the rubber modified thermoplastic resin comprises structural units derived from at least one vinyl aromatic monomer, at least one monoethylenically unsaturated nitrile monomer, and at least one monomer selected from the group consisting of ( $C_1$ - $C_{12}$ )alkyl- and aryl- (meth)acrylate monomers. Suitable ( $C_1$ - $C_{12}$ )alkyl- and aryl-(meth)acrylate monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers include those set forth hereinabove in the description of the rubber substrate. In a particular embodiment the rigid thermoplastic phase comprises a vinyl aromatic polymer having first structural units derived from one or more vinyl aromatic monomers; second structural units derived from one or more monoethylenically unsaturated nitrile monomers; and third structural units derived from one or more monomers selected from the group consisting of ( $C_1$ - $C_{12}$ )alkyl- and aryl- (meth)acrylate monomers. Suitable vinyl aromatic polymers comprise at least about 20 wt.% structural units derived from one or more vinyl aromatic monomers. Examples of such vinyl aromatic polymers include, but are not limited to, styrene/acrylonitrile/methyl methacrylate copolymer, alpha-methylstyrene/acrylonitrile/methyl methacrylate copolymer and styrene/alpha-methylstyrene/acrylonitrile/methyl methacrylate copolymer. These copolymers may be used for the rigid thermoplastic phase either individually or as mixtures.

[0027] When structural units in copolymers are derived from one or more monoethylenically unsaturated nitrile monomers, then the nitrile monomer content in the copolymer comprising the graft copolymer and the rigid thermoplastic phase may be in one embodiment in a range of between about 5 and about 40 percent by weight, in another embodiment in a range of between about 5 and about 30 percent by weight, in another embodiment in a range of between about 10 and about 30 percent by weight, and in yet another embodiment in a range of between about 15 and about 30

percent by weight, based on the weight of the copolymer comprising the graft copolymer and the rigid thermoplastic phase.

[0028] The amount of grafting that takes place between the rubber phase and monomers comprising the rigid thermoplastic phase of the rubber modified thermoplastic resin varies with the relative amount and composition of the rubber phase. In one embodiment, greater than about 10 wt.% of the rigid thermoplastic phase is chemically grafted to the rubber, based on the total amount of rigid thermoplastic phase in the composition. In another embodiment, greater than about 15 wt.% of the rigid thermoplastic phase is chemically grafted to the rubber, based on the total amount of rigid thermoplastic phase in the composition. In still another embodiment, greater than about 20 wt.% of the rigid thermoplastic phase is chemically grafted to the rubber, based on the total amount of rigid thermoplastic phase in the composition. In particular embodiments the amount of rigid thermoplastic phase chemically grafted to the rubber may be in a range of between about 5% and about 90 wt.%; between about 10% and about 90 wt.%; between about 15% and about 85 wt.%; between about 15% and about 50 wt.%; or between about 20% and about 50 wt.%, based on the total amount of rigid thermoplastic phase in the composition. In yet other embodiments, about 40 to 90 wt.% of the rigid thermoplastic phase is free, that is, non-grafted.

[0029] The rigid thermoplastic phase of the rubber modified thermoplastic resin may be present in compositions of the invention in one embodiment at a level of from about 85 to about 6 percent by weight; in another embodiment at a level of from about 65 to about 6 percent by weight; in another embodiment at a level of from about 60 to about 20 percent by weight; in another embodiment at a level of from about 75 to about 40 percent by weight, and in still another embodiment at a level of from about 60 to about 50 percent by weight based on the weight of the rubber modified thermoplastic resin. In other embodiments rigid thermoplastic phase may be present in compositions of the invention in a range of between about 90% and about 30 wt.%, based on the weight of the rubber modified thermoplastic resin.

[0030] The rigid thermoplastic phase of the rubber modified thermoplastic resin may be formed solely by polymerization carried out in the presence of rubber substrate or by addition of one or more separately polymerized rigid thermoplastic polymers to a rigid thermoplastic polymer that has been polymerized in the presence of the rubber substrate. When at least a portion of separately synthesized rigid thermoplastic phase is added to compositions, then the amount of said separately synthesized rigid

thermoplastic phase added is in an amount in a range of between about 30 wt. % and about 80 wt. % based on the weight of the rubber modified thermoplastic resin. Two or more different rubber substrates each possessing a different number average particle size may be separately employed in such a polymerization reaction and then the products blended together. In illustrative embodiments wherein such products each possessing a different number average particle size of initial rubber substrate are blended together, then the ratios of said substrates may be in a range of about 90:10 to about 10:90, or in a range of about 80:20 to about 20:80, or in a range of about 70:30 to about 30:70. In some embodiments an initial rubber substrate with smaller particle size is the major component in such a blend containing more than one particle size of initial rubber substrate.

[0031] The rigid thermoplastic phase of the rubber modified thermoplastic resin may be made according to known processes, for example, mass polymerization, emulsion polymerization, suspension polymerization or combinations thereof, wherein at least a portion of the rigid thermoplastic phase is chemically bonded, i.e., "grafted" to the rubber phase via reaction with unsaturated sites present in the rubber phase. The grafting reaction may be performed in a batch, continuous or semi-continuous process. Representative procedures include, but are not limited to, those taught in U.S. Patent Nos. 3,944,631; and U.S. patent application Serial No. 08/962,458, filed October 31, 1997. The unsaturated sites in the rubber phase are provided, for example, by residual unsaturated sites in those structural units of the rubber that were derived from a graftlinking monomer.

[0032] In some embodiments of the present invention the rubber modified thermoplastic resin is made by a process which comprises monomer grafting to rubber substrate with concomitant formation of rigid thermoplastic phase, which process is performed in stages wherein at least one first monomer is grafted to rubber substrate followed by at least one second monomer different from said first monomer. In the present context the change from one graft stage to the next is defined as that point where there is a change in the identity of at least one monomer added to the rubber substrate for grafting. In one embodiment of the present invention formation of rigid thermoplastic phase and grafting to rubber substrate are performed by feeding at least one first monomer over time to a reaction mixture comprising rubber substrate. In this context a second graft stage occurs when at least one different monomer is introduced into the feed stream in the presence or absence of at least one first monomer.

[0033] At least two stages are employed for grafting, although additional stages may be employed. The first graft stage is performed with one or more monomers comprising vinyl aromatic monomers, monoethylenically unsaturated nitrile monomers, and optionally (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers. In a particular embodiment grafting is performed in a first stage with a mixture of monomers, at least one of which is selected from the group consisting of vinyl aromatic monomers and at least one of which is selected from the group consisting of monoethylenically unsaturated nitrile monomers. When a mixture comprising at least one vinyl aromatic monomer and at least one monoethylenically unsaturated nitrile monomer is employed in the first graft stage, then the wt./wt. ratio of vinyl aromatic monomer to monoethylenically unsaturated nitrile monomer is in one embodiment in a range of between about 1:1 and about 6:1, in another embodiment in a range of between about 1.5:1 and about 4:1, in still another embodiment in a range of between about 2:1 and about 3:1, and in still another embodiment in a range of between about 2.5:1 and about 3:1. In one preferred embodiment the wt./wt. ratio of vinyl aromatic monomer to monoethylenically unsaturated nitrile monomer employed in the first graft stage is about 2.6:1.

[0034] In at least one subsequent stage following said first stage, grafting is performed with one or more monomers comprising vinyl aromatic monomers, monoethylenically unsaturated nitrile monomers, and optionally (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers. In a particular embodiment grafting is performed in at least one subsequent stage with one or more monomers, at least one of which is selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers. In another particular embodiment grafting is performed in at least one subsequent stage with a mixture of monomers, at least one of which is selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers and at least one of which is selected from the group consisting of vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers. In another particular embodiment grafting is performed in at least one subsequent stage with a mixture of monomers, one of which is selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers; one of which is selected from the group consisting of vinyl aromatic monomers and one of which is selected from the group consisting of monoethylenically unsaturated nitrile monomers. Said (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers include those described hereinabove.

[0035] In the first graft stage the total amount of monomer employed for grafting to rubber substrate is in one embodiment in a range of between about 5 wt.% and about 98 wt.%; in another embodiment in a range of between about 5 wt.% and about 95 wt.%; in another embodiment in a range of between about 10 wt.% and about 90 wt.%; in another embodiment in a range of between about 15 wt.% and about 85 wt.%; in another embodiment in a range of between about 20 wt.% and about 80 wt.%; and in yet another embodiment in a range of between about 30 wt.% and about 70 wt.%, based on the total weight of monomer employed for grafting in all stages. In one particular embodiment the total amount of monomer employed for grafting to rubber substrate in the first stage is in a range of between about 30 wt.% and about 95 wt.% based on the total weight of monomer employed for grafting in all stages. Further monomer is then grafted to rubber substrate in one or more stages following said first stage. In one particular embodiment all further monomer is grafted to rubber substrate in one second stage following said first stage.

[0036] At least one (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomer is employed for grafting to rubber substrate in either a first stage, or in a second stage, or in both a first and a second stage of grafting monomers to rubber substrate. The total amount of said (meth)acrylate monomer employed is in one embodiment in a range of between about 95 wt.% and about 2 wt.%; in another embodiment in a range of between about 80 wt.% and about 2 wt.%; in another embodiment in a range of between about 70 wt.% and about 2 wt.%; in another embodiment in a range of between about 50 wt.% and about 2 wt.%; in another embodiment in a range of between about 45 wt.% and about 2 wt.%; and in yet another embodiment in a range of between about 45 wt.% and about 5 wt.%, based on the total weight of all monomers employed for grafting. In other embodiments of the invention the total amount of said (meth)acrylate monomer employed is in a range of between about 48 wt.% and about 18 wt.%.

[0037] In a mixture of monomers comprising at least one (C<sub>1</sub>-C<sub>12</sub>)alkyl- and aryl-(meth)acrylate monomer, the wt./wt. ratio of said (meth)acrylate monomer to the totality of other monomers employed for grafting to rubber substrate in any particular stage is in one embodiment in a range of between about 10:1 and about 1:10; in another embodiment in a range of between about 8:1 and about 1:8; in another embodiment in a range of between about 5:1 and about 1:5; in another embodiment in a range of between about 4:1 and about 1:4; in another embodiment in a range of between about 3:1 and about 1:3; in another embodiment in a range of between about



2:1 and about 1:2; and in yet another embodiment in a range of between about 1.5:1 and about 1:1.5.

[0038] Optionally, at least one additional thermoplastic resin different from the polycarbonate may be present in the compositions of the invention. Illustrative additional thermoplastic resins comprise those selected from the group consisting of (meth)acrylate homopolymers and copolymers, methyl methacrylate-butyl acrylate copolymer, methyl methacrylate-ethyl acrylate copolymer, styrene and alkylstyrene homopolymers and copolymers, styrene-acrylonitrile (SAN) copolymer, alpha-methylstyrene-acrylonitrile (AMSAN) copolymer, methyl methacrylate-styrene-acrylonitrile (MMA-SAN) terpolymer, methyl methacrylate/alpha-methylstyrene/acrylonitrile (MMA-AMSAN) terpolymer, and mixtures thereof. In some embodiments the additional thermoplastic resin different from polycarbonate is identical to or is present in addition to the separately polymerized rigid thermoplastic polymers referred to herein above. When present, the additional thermoplastic resin is present in the composition in a range of between about 1 wt.% and about 80 wt.%, or in a range of between about 20 wt.% and about 70 wt.%, or in a range of between about 25 wt.% and about 60 wt.%, based on the weight of the entire composition

[0039] Compositions of the present invention may optionally comprise conventional additives known in the art including, but not limited to, stabilizers, such as color stabilizers, heat stabilizers, light stabilizers, antioxidants, and UV stabilizers; neutralizers; flame retardants, anti-drip agents, lubricants, flow promoters and other processing aids; plasticizers, antistatic agents, mold release agents, impact modifiers, fillers, and colorants such as dyes and pigments which may be organic, inorganic or organometallic; and like additives. Illustrative additives include, but are not limited to, silica, silicates, zeolites, titanium dioxide, stone powder, glass fibers or spheres, carbon fibers, carbon black, conductive carbon black, graphite, calcium carbonate, talc, mica, lithopone, zinc oxide, zirconium silicate, iron oxides, diatomaceous earth, calcium carbonate, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, clay, calcined clay, organoclay, talc, kaolin, asbestos, cellulose, wood flour, cork, cotton and synthetic textile fibers, reinforcing fillers, glass fibers, carbon fibers, conductive carbon fibers, carbon nanotubes, and metal fibers. Often more than one additive is included in compositions of the invention, and in some embodiments more than one additive of one type is included. In a particular embodiment a composition further comprises an additive selected from the group

consisting of colorants, dyes, pigments, lubricants, mold release agents, stabilizers, fillers and mixtures thereof.

[0040] In another embodiment the present invention comprises methods for making the compositions disclosed herein. The compositions may be made by combining and intimately mixing the components of the composition under conditions suitable for the formation of a blend of the components, illustrative examples of which include, but are not limited to, melt mixing using, for example, a two-roll mill, a kneader, a Banbury mixer, a disc-pack processor, a single screw extruder or a co-rotating or counter-rotating twin-screw extruder, and then reducing the composition so formed to particulate form, for example by pelletizing or grinding the composition. Because of the availability of melt blending equipment in commercial polymer processing facilities, melt processing procedures are generally preferred. When compositions are prepared by extrusion, they may be prepared by using a single extruder having multiple feed ports along its length to accommodate the addition of the various components at different points in the mixing process. It is also sometimes advantageous to employ at least one vent port in each section between the feed ports to allow venting (either atmospheric or vacuum) of the melt. Those of ordinary skill in the art will be able to adjust blending times and temperatures, as well as component addition location and sequence, without undue additional experimentation.

[0041] The compositions of the present invention can be formed into useful articles. In some embodiments the articles are unitary articles comprising a composition of the present invention. In other embodiments the articles may comprise a multilayer article comprising at least one layer comprising a composition of the present invention.

[0042] Multilayer and unitary articles which can be made which comprise compositions made by the method of the present invention include, but are not limited to, articles for outdoor vehicle and device (OVAD) applications; exterior and interior components for aircraft, automotive, truck, military vehicle (including automotive, aircraft, and water-borne vehicles), scooter, and motorcycle, including panels, quarter panels, rocker panels, vertical panels, horizontal panels, trim, pillars, center posts, fenders, doors, decklids, trunklids, hoods, bonnets, roofs, bumpers, fascia, grilles, mirror housings, pillar appliques, cladding, body side moldings, wheel covers, hubcaps, door handles, spoilers, window frames, headlamp bezels and housings, tail lamp housings, tail lamp bezels, license plate enclosures, roof racks, and running boards; enclosures, housings, panels, and parts for outdoor vehicles and devices;

enclosures for electrical and telecommunication devices; outdoor furniture; aircraft components; boats and marine equipment, including trim, enclosures, and housings; outboard motor housings; depth finder housings, personal water-craft; jet-skis; pools; spas; hot-tubs; steps; step coverings; building and construction applications such as glazing, fencing, decking planks, roofs; siding, particularly vinyl siding applications; windows, floors, decorative window furnishings or treatments; wall panels, and doors; outdoor and indoor signs; enclosures, housings, panels, and parts for automatic teller machines (ATM); enclosures, housings, panels, and parts for lawn and garden tractors, lawn mowers, and tools, including lawn and garden tools; window and door trim; sports equipment and toys; enclosures, housings, panels, and parts for snowmobiles; recreational vehicle panels and components; playground equipment; articles made from plastic-wood combinations; golf course markers; utility pit covers; mobile phone housings; radio sender housings; radio receiver housings; light fixtures; light switches; electrical sockets; lighting appliances; reflectors; network interface device housings; transformer housings; air conditioner housings; cladding or seating for public transportation; cladding or seating for trains, subways, or buses; meter housings; antenna housings; cladding for satellite dishes; and like applications. Said articles may be prepared by a variety of known processes and fabrication steps which include, but are not limited to, profile extrusion, sheet extrusion, coextrusion, extrusion blow molding, thermoforming, injection molding, compression molding, in-mold decoration, baking in a paint oven, plating, and lamination.

[0043] Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following examples are included to provide additional guidance to those skilled in the art in practicing the claimed invention. The examples provided are merely representative of the work that contributes to the teaching of the present application. Accordingly, these examples are not intended to limit the invention, as defined in the appended claims, in any manner.

[0044] In the following examples Vicat B data at 120°C were determined according to ISO 306. Flex plate impact strength was determined according to ISO 6603/2. Notched Izod impact strength was determined according to ISO 180/1A. Melt volume rate (MVR) at 260°C was determined on granulate using a 5 kilogram weight according to ISO 1133.

## EXAMPLES 1-5

[0045] The following examples illustrate preparation of rubber modified thermoplastic resin by staged feeding of monomers for grafting as is described in pending U.S. patent application Serial No. 10/748,394, filed December 30, 2003. Agitated reaction mixtures comprising 212.8 parts demineralized water and 45 parts of a PBA with broad particle size distribution were heated to 60°C. Various amounts of a monomer mixture consisting of styrene and acrylonitrile (2:1 wt/wt ratio) were fed to each reaction in a first stage while various amounts of a monomer mixture consisting of styrene, acrylonitrile and methyl methacrylate (40:25:35 wt/wt/wt ratio) were fed to each reaction in a second stage. The monomer feed times were adjusted according to the relative amounts of monomer being fed so as to keep the overall monomer flow rates constant at 55 parts total monomer being added continuously over 90 minutes. In addition 0.225 parts cumene hydroperoxide and an activator solution of 5 parts demineralized water, 0.0033 parts ferric sulfate heptahydrate, 0.3 parts sodium formaldehyde sulfoxylate and 0.0165 parts disodium salt of ethylene diamine tetraacetic acid were fed continuously to each reaction mixture over 125 minutes. The final products comprising rigid thermoplastic phase and grafted rubber substrate were coagulated with aqueous calcium chloride and dried in a fluid bed dryer at 70°C. Table 1 shows the parts by weight (pbw) of monomer fed to each reaction mixture. All values for wt. % gel represent the acetone-insoluble portion of the product, which typically comprises PBA and any additional monomer species grafted to PBA.

TABLE 1

Example	1	2	3	4	5
1 <sup>st</sup> Stage monomer					
styrene	6.11	12.22	18.34	24.45	30.56
acrylonitrile	3.06	6.11	9.17	12.22	15.28
2 <sup>nd</sup> Stage monomer					
styrene	18.33	14.67	11	7.33	3.67
acrylonitrile	11.46	9.17	6.87	4.58	2.29
methyl methacrylate	16.04	12.83	9.62	6.42	3.21
Wt. % Gel in product	50.5	51	54	59	63

## EXAMPLES 6-9

[0046] Preparations of rubber modified thermoplastic resin by staged feeding of monomers for grafting were run in which 45 parts by weight of a poly(butyl acrylate) (PBA) rubber substrate was grafted in two stages with 55 parts by weight of a monomer mixture comprising various % ratios (wt./wt./wt. totaling 100) of styrene-acrylonitrile-methyl methacrylate under conditions similar to those described for Examples 1-5. The rubber substrate in each case was prepared by a continuous procedure and comprised a broad rubber particle size distribution. Table 2 shows the amounts of styrene, acrylonitrile and methyl methacrylate employed in each graft reaction at each stage and characterization data for the resulting product.

TABLE 2

Example	6	7	8	9
1 <sup>st</sup> Stage monomer				
Parts styrene	12.1	12.1	16.59	20.27
Parts acrylonitrile	4.54	4.54	7.53	9.98
Parts MMA	13.61	13.61	6.12	0
2 <sup>nd</sup> Stage monomer				
Parts styrene	9.9	16.58	13.58	9.9
Parts acrylonitrile	3.71	8.17	6.16	3.71
Parts MMA	11.14	0	5.01	11.14
Wt. % Gel in product	55	60.6	60.6	64.6

## EXAMPLE 10

[0047] The preparation of rubber modified thermoplastic resin was performed under conditions similar to those of Example 9 except that 45 parts of a PBA with 475nm number average particle size was employed. Also, a dimer fatty acid surfactant was employed and the final product comprising rigid thermoplastic phase and grafted rubber substrate was coagulated with sulfuric acid.

## EXAMPLE 11

[0048] The preparation of rubber modified thermoplastic resin was performed under conditions similar to those of Example 9 except that 45 parts of a PBA with 90nm number average particle size was employed. Also, a dimer fatty acid surfactant was employed and the final product comprising rigid thermoplastic phase and grafted rubber substrate was coagulated with sulfuric acid.

## EXAMPLE 12

[0049] The preparation of rubber modified thermoplastic resin was performed under conditions similar to those of Example 9 except that 45 parts of a PBA with 475nm number average particle size was employed. Also, sodium lauryl sulfate surfactant was employed (for example, using a method similar to that described in European Patent Application EP0913408) and the final product comprising rigid thermoplastic phase and grafted rubber substrate was coagulated with calcium chloride.

## EXAMPLE 13

[0050] The preparation of rubber modified thermoplastic resin was performed under conditions similar to those of Example 9 except that 45 parts of a PBA with 90nm number average particle size was employed. Also, sodium lauryl sulfate surfactant was employed and the final product comprising rigid thermoplastic phase and grafted rubber substrate was coagulated with calcium chloride.

## EXAMPLE 14

[0051] A preparation of rubber modified thermoplastic resin by staged feeding of monomers for grafting was run in which 45 parts by weight of a poly(butyl acrylate) (PBA) rubber substrate was grafted in two stages with 55 parts by weight of a monomer mixture comprising various % ratios (wt./wt./wt. totaling 100) of styrene-acrylonitrile-methyl methacrylate. The rubber substrate was prepared by a continuous

procedure and comprised a broad rubber particle size distribution. In the first stage the rubber was grafted with 22.69 pbw styrene and 7.56 pbw acrylonitrile. In the second stage the rubber was grafted with 9.9 pbw styrene, 3.71 pbw acrylonitrile and 11.14 pbw methyl methacrylate. A rubber modified thermoplastic resin was obtained.

#### EXAMPLES 15-20

[0052] Preparations of rubber modified thermoplastic resin by staged feeding of monomers for grafting were run in which 45 parts by weight of a poly(butyl acrylate) (PBA) rubber substrate was grafted in two stages with 55 parts by weight of a monomer mixture comprising various % ratios (wt./wt./wt. totaling 100) of styrene-acrylonitrile-methyl methacrylate under conditions similar to those described for Examples 1-5. The PBA employed was a blend of 100nm mean particle size PBA and 500nm mean particle size PBA in a 70:30 ratio, respectively. Table 3 shows the amounts of styrene, acrylonitrile and methyl methacrylate employed in each graft reaction at each stage.

TABLE 3

Example	15	16	17	18	19	20
1 <sup>st</sup> Stage monomer						
styrene	20.44	20.44	20.44	21.96	21.96	21.96
acrylonitrile	10.07	10.07	10.07	8.54	8.54	8.54
2 <sup>nd</sup> Stage monomer						
styrene	9.80	9.80	7.35	9.80	9.80	7.35
acrylonitrile	6.13	3.68	2.45	6.13	3.68	2.45
methyl methacrylate	8.58	11.03	14.70	8.58	11.03	14.70

#### EXAMPLES 21-25 AND COMPARATIVE EXAMPLE

[0053] Compositions comprising 33 parts by weight bisphenol A polycarbonate (with a weight average molecular weight relative to polystyrene standards in a range of between about 28,000 to about 36,000 g/mol) and 40 parts by weight of a suspension-prepared SAN (derived from 75% styrene and 25% acrylonitrile) were combined with 27 parts by weight of various rubber modified thermoplastic resins prepared by staged feeding of monomers for grafting. In addition all the compositions comprised 4 parts by weight of a copolymer derived from methyl methacrylate and butyl acrylate; 1.28

parts by weight of mold release agents, heat stabilizers and UV screeners; 12 parts by weight coated titanium dioxide; and 0.1 parts by weight of other pigments. Compositions in the examples were prepared by dry blending components in a mixer following by extrusion using typical processing equipment at around 200-250°C. The extrudates were pelletized, dried and molded at different melt temperatures. Table 4 shows the various rubber modified thermoplastic resins prepared by staged feeding of styrene, acrylonitrile and methyl methacrylate monomers for grafting (referred to as M-ASA-graft). A comparative example (C.Ex.) was prepared which had the same composition as the other examples except that it employed a rubber modified thermoplastic resin (referred to as ASA) prepared by grafting 45 pbw poly(butyl acrylate) with 36.5 pbw styrene and 19 pbw acrylonitrile in a single stage. Test specimens were molded at 255°C melt temperature and also at 300°C melt temperature to stimulate abusive conditions. The molded test specimens were subjected to color measurements in the CIE L\*a\*b\* space using a MacBeth 7000 spectrophotometer for color measurement. Values for delta E showing the difference in color between specimens molded at 255°C and at 300°C are given in Table 4. Selected physical properties for test specimens molded at 255°C (unless noted) are also shown in Table 4.

TABLE 4

Example	C.Ex.	21	22	23	24	25
M-ASA-graft	ASA	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 14
delta E	3.39	0.98	2.19	1.36	1.45	0.96
60° Gloss*	79	89	86	91	90	93
Vicat B, °C	108	106.5	107.4	107.3	108	107.5
Flex plate impact, Joules	14.7	17.6	18.7	20.9	11.9	21.9
Izod impact, kJ/m <sup>2</sup>	11.8	8.7	10.2	11.7	11.8	11.0
MVR, cm <sup>3</sup> /10min.	23.2	28	25.6	24	23.8	24.8

\*determined on parts molded at 300°C

[0054] The data show that compositions containing rubber modified thermoplastic resins comprising structural units derived from methyl methacrylate possess better color properties and gloss upon exposure to elevated temperatures than does a control containing rubber modified thermoplastic resin prepared without structural units derived from methyl methacrylate.



## EXAMPLES 26-29 AND COMPARATIVE EXAMPLE

[0055] Compositions were prepared as described in Examples 21-25 with similar amounts of components. Table 5 shows the various rubber modified thermoplastic resins prepared by staged feeding of styrene, acrylonitrile and methyl methacrylate monomers for grafting (referred to as M-ASA-graft). A comparative example (C.Ex.) was prepared which had the same composition as the other examples except that it employed a rubber modified thermoplastic resin (referred to as ASA) prepared by grafting 45 pbw poly(butyl acrylate) with 36.5 pbw styrene and 19 pbw acrylonitrile in a single stage. Test specimens were molded at 255°C melt temperature and also at 300°C melt temperature to simulate abusive conditions. The molded test specimens were subjected to color measurements in the CIE L\*a\*b\* space using a MacBeth 7000 spectrophotometer for color measurement. Values for delta E showing the difference in color between specimens molded at 255°C and at 300°C are given in Table 5. Selected physical properties for test specimens molded at 255°C (unless noted) are also shown in Table 5.

TABLE 5

Example	C.Ex.	26	27	28	29
M-ASA-graft	ASA	Ex. 10	Ex. 11	Ex. 12	Ex. 13
delta E	3.39	1.29	0.80	1.38	1.22
60° Gloss*	79	96	86	95	88
Vicat B, °C	108	107.2	107.4	107.7	107.8
Flex plate impact, Joules	14.7	8.4	47.9	18	23
Izod impact, kJ/m <sup>2</sup>	11.8	11.5	12.2	10	11.8
MVR, cm <sup>3</sup> /10min.	23.2	21.9	18.3	23.0	13.6

\*determined on parts molded at 300°C

[0056] The data show that compositions containing rubber modified thermoplastic resins comprising structural units derived from methyl methacrylate possess better color properties and gloss upon exposure to elevated temperatures than does a control containing rubber modified thermoplastic resin prepared without structural units derived from methyl methacrylate.

## EXAMPLES 30-32 AND COMPARATIVE EXAMPLE

[0057] Compositions were prepared as described in Examples 15-19 with similar amounts of components except that 40 parts by weight of various thermoplastic resins were added in place of 40 parts by weight of a suspension-prepared SAN derived from 75% styrene and 25% acrylonitrile. The various thermoplastic resins were a terpolymer derived from 40% styrene, 25% acrylonitrile and 35% methyl methacrylate (designated "MMA-SAN"); a copolymer derived from 30% alpha-methyl styrene and 70% acrylonitrile (designated "AMSAN"); and a copolymer derived from 66% styrene and 34% acrylonitrile (designated "SAN 66:33"). Each composition comprised 27 parts by weight of the rubber modified thermoplastic resin of Example 9. Table 6 shows the identity of the added thermoplastic resin. A comparative example (C.Ex.) was prepared which had the same composition as the other examples except that it employed 40 parts by weight of a suspension-prepared SAN (derived from 75% styrene and 25% acrylonitrile and designated "SAN 75:25") and a rubber modified thermoplastic resin (referred to as ASA) prepared by grafting 45 pbw poly(butyl acrylate) with 36.5 pbw styrene and 19 pbw acrylonitrile in a single stage. Test specimens were molded at 255°C melt temperature and also at 300°C melt temperature to stimulate abusive conditions. The molded test specimens were subjected to color measurements in the CIE L\*a\*b\* space using a MacBeth 7000 spectrophotometer for color measurement. Values for delta E showing the difference in color between specimens molded at 255°C and at 300°C are given in Table 6. Selected physical properties for test specimens molded at 255°C (unless noted) are also shown in Table 6.

TABLE 6

Example	C.Ex.	30	31	32
Thermoplastic resin	SAN 75:25	MMA-SAN	AMSAN	SAN 66:33
delta E	3.39	1.30	1.34	1.95
60° Gloss*	79	90	90	90
Vicat B, °C	108	100.9	117.5	108.9
Flex plate impact, Joules	14.7	43.5	49.6	37.4
Izod impact, kJ/m <sup>2</sup>	11.8	17.6	19.8	18.9
MVR, cm <sup>3</sup> /10min.	23.2	10.6	6.9	14.6

\*determined on parts molded at 300°C

[0058] The data show that compositions containing rubber modified thermoplastic resins comprising structural units derived from methyl methacrylate possess better color properties and gloss upon exposure to elevated temperatures than does a control containing rubber modified thermoplastic resin prepared without structural units derived from methyl methacrylate.

#### EXAMPLE 33 AND COMPARATIVE EXAMPLE

[0059] A composition was prepared comprising the following components: 18 pbw bisphenol A polycarbonate with a weight average molecular weight relative to polystyrene standards in a range of between about 18,000 and about 23,000 g/mol; 42 pbw bisphenol A polycarbonate with a weight average molecular weight relative to polystyrene standards in a range of between about 28,000 and about 36,000 g/mol; and 22 parts by weight of a suspension-prepared SAN (derived from 75% styrene and 25% acrylonitrile). The composition further comprised 18 parts by weight of a rubber modified thermoplastic resin prepared as in Example 9. In addition the composition comprised 0.5 parts by weight of mold release agents and heat stabilizers; 12 parts by weight coated titanium dioxide; and 0.1 parts by weight of other pigments. Compositions in the examples were prepared by dry blending components in a mixer following by extrusion using typical processing equipment. The extrudates were pelletized, dried and molded. A comparative example (C.Ex.) was prepared which had the same composition except that it employed a rubber modified thermoplastic resin (referred to as ASA) prepared by grafting 45 pbw poly(butyl acrylate) with 36.5 pbw styrene and 19 pbw acrylonitrile in a single stage. Test specimens were molded at 260°C melt temperature and also at 320°C melt temperature to simulate abusive conditions. The molded test specimens were subjected to color measurements in the CIE L\*a\*b\* space using a MacBeth 7000 spectrophotometer for color measurement. Values for delta E showing the difference in color between specimens molded at 260°C and at 320°C were 3.33 for the comparative example and 1.59 for the example containing the rubber modified thermoplastic resin prepared as in Example 9.

#### EXAMPLE 34 AND COMPARATIVE EXAMPLE

[0060] A composition was prepared comprising the following components: 50 pbw bisphenol A polycarbonate with a weight average molecular weight relative to polystyrene standards in a range of between about 28,000 and about 36,000 g/mol; 27 pbw bisphenol A polycarbonate with a weight average molecular weight relative to polystyrene standards in a range of between about 18,000 and about 23,000 g/mol;

and 9.5 parts by weight of a suspension-prepared SAN (derived from 75% styrene and 25% acrylonitrile). The composition further comprised 13.5 parts by weight of a rubber modified thermoplastic resin prepared as in Example 9. In addition the composition comprised 0.5 parts by weight of mold release agents and heat stabilizers; 12 parts by weight coated titanium dioxide; and 0.1 parts by weight of other pigments. Compositions in the examples were prepared by dry blending components in a mixer followed by extrusion using typical processing equipment. The extrudates were pelletized, dried and molded. A comparative example (C.Ex.) was prepared which had the same composition except that it employed a rubber modified thermoplastic resin (referred to as ASA) prepared by grafting 45 pbw poly(butyl acrylate) with 36.5 pbw styrene and 19 pbw acrylonitrile in a single stage. Test specimens were molded at 260°C melt temperature and also at 320°C melt temperature to simulate abusive conditions. The molded test specimens were subjected to color measurements in the CIE L\*a\*b\* space using a MacBeth 7000 spectrophotometer for color measurement. Values for delta E showing the difference in color between specimens molded at 260°C and at 320°C were 3.34 for the comparative example and 1.78 for the example containing the rubber modified thermoplastic resin prepared as in Example 9.

[0061] While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present invention. As such, further modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims. All Patents and Patent Applications cited herein are incorporated herein by reference.